New integrated photocatalytic-biological flow system using supported TiO\(_2\) and fixed bacteria for the mineralization of isoproturon

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Abstract

The photodegradation of isoproturon (IP) was performed using TiO\(_2\) supported on glass rings in a 1.5 l coaxial reactor. After 60 min of phototreatment, IP was completely eliminated and about 80% of dissolved organic carbon (DOC) remained in solution. This efficiency of photodegradation was compared with that using the suspended catalyst in solution and the results indicated that the catalytic activity of TiO\(_2\) is not reduced when it is immobilized. The durability of the supported TiO\(_2\) was also tested. It was found that after 300 h of photodegradation experiments, its activity was not affected. The chemical nature of the phototreated solution was assessed following the evolution of the initial compound, the organic carbon, and the formed ions, as well as the toxicity and the biodegradability. These analyses demonstrated that the solution resulting from the phototreatment of IP is biologically compatible and its complete mineralization can be performed by biological means. In this way, for the mineralization of an IP solution, a combined photochemical and biological flow reactor was used operating in semi-continuous mode at laboratory scale. This coupled system employs TiO\(_2\) supported on glass rings in the photocatalytic reactor and bacteria supported on biolite in the biological part. In this combined system, 100% of the initial concentration of IP and 95% of DOC were removed. Finally, some field experiments under direct sunlight were carried out at the Plataforma Solar de Almería (PSA), Spain. The photocatalytic oxidation of IP was performed in homogeneous and heterogeneous solutions and two different reactors were compared: a medium concentrating radiation system (Helioman, HM) and a non-concentrating radiation system (compound parabolic collectors, CPC). The degradation rates obtained in the CPC are around 5 times more efficient than the HM collectors. However, in both systems 100% of the initial concentration of IP was removed. The possibility of coupling a CPC photoreactor with a biological system at field pilot scale employing supported TiO\(_2\) and fixed bacteria for the treatment of real bio-recalcitrant wastewater is also suggested. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Water detoxification; Photochemical treatment; Supported TiO\(_2\); Fixed bacteria; Isoproturon; Coupled flow reactor; Integrated chemical-biological treatment; Toxicity; Biodegradability; Solar application
1. Introduction

Isoproturon (IP) is one of the most used herbicides in Europe [1] and it is often found in contaminated groundwater [2], surface water [3], and effluents of wastewater treatment plants [4]. This fact indicates that this herbicide is difficult to eliminate by a conventional biological wastewater treatment process. The non-biodegradability of this herbicide has been proved in our laboratory [5]. Traditionally, herbicides in water are removed using granular or powdered activated carbon, by nanofiltration, ozonation, or by isolation of specific bacterial cultures [6], but these processes have inherent limitations in applicability, effectiveness, and costs.

Advanced oxidation processes (AOP), such as TiO₂ photocatalysis, have been considered as the most promising methods for the remediation of contaminated water [7]. The efficiency of these systems is based on the production of strong oxidant species, such as hydroxyl radicals, which are able to oxidize almost all organic pollutants. The photo-assisted catalysis involves the irradiation of a semiconductor like TiO₂ with UV light at \( \lambda \) below 387 nm, generating electron–hole pair on the catalyst surface and inducing the formation of radical reduced oxygen species. These radicals are produced in situ and are highly reactive and indiscriminate oxidants. Such reactions have usually been carried out using suspensions of powdered TiO₂. The inconvenience of this kind of approach at large scale is the catalyst-recovering step from the solution at the end of the operation. This problem can be solved immobilizing the catalyst on an inert surface without activity losses. Many works have been reported based on supported TiO₂ catalysts [8–10]. In these works, a variety of supporting materials, coating methods, and reactor arrangements have been investigated from both engineering and fundamental points of view.

Even using fixed and active TiO₂, the operational costs of these AOPs for the total oxidation of hazardous organic compounds or non-biodegradable effluents remain relatively high compared to those of a biological treatment. However, their use as a pre-treatment step to enhance the biodegradability of wastewater containing recalcitrant or inhibitory compounds can potentially be justified if the resulting intermediates are easily degradable by microorganisms in a further biological treatment. Many reports have been focused in the search of new oxidation technologies as pre-treatment for effluents before biological conventional treatments. These studies attempt some form of combined chemical-oxidation and biological processes to treat contaminants in wastewater [11–13]. The chemical processes utilized include: ozone [14], ozone/hydrogen peroxide [15], hydrogen peroxide/UV [16], an electron beam with and without oxygen and hydrogen peroxide [17], UV light [18], wet air oxidation [19], artificial sunlight [20], and Fenton reaction [21], among others. These results, mainly from laboratory studies, suggest potential advantages for water treatment.

The main research topic of our group aims to combine physicochemical and biological treatment processes to mineralize toxic and/or bio-recalcitrant compounds. In precedents works we developed a coupled photochemical-biological reactor, which uses a photo-Fenton pre-treatment, followed by a biological system with immobilized biomass [5,22]. In the present paper, we present the development of a new-coupled system employing TiO₂ supported on glass rings in the photocatalytic reactor and bacteria supported on biofilm in the biological part. The advantages of this system are that the catalyst can be re-used and the pH of the solution remains at values between 6.0 and 6.5, which are tolerable by the biomass. The photo-Fenton reaction instead, renders the phototreated solution acidic making neutralization necessary.

Our coupled photochemical and biological flow reactor is employed to reach the complete mineralization of IP. Preliminaries experiments concerning the chemical and biological characteristics of phototreated solutions were carried out to determine the moment when the phototreated solution becomes biocompatible.

The following topics are also studied in this paper: (a) the comparison of suspended and supported TiO₂ for the degradation of IP, (b) the supported TiO₂ durability, (c) the effect of the structure of 4 different phenyl-urea herbicides on their photodegradation via TiO₂, (d) comparison of different AOP at pilot scale, (e) the efficiency of degradation in a large plant by direct solar light and (f) the feasibility of coupling a compound parabolic collector (CPC) with a biological system at field pilot scale employing supported TiO₂ and fixed bacteria for the treatment of real bio-recalcitrant wastewater.
2. Experimental

2.1. Materials

All chemical products were used as received. Metribromuron (MB), chlorotoluron (CT), chlorbromuron (CB), and IP were obtained from Ciba (Monthey, Switzerland); Fig. 1 shows the chemical structure of the herbicides studied. TiO$_2$ was Degussa P-25, mainly anatase with a surface area of 50 m$^2$ g$^{-1}$. The glass rings with supported TiO$_2$ (Degussa P-25) were provided by the Laboratory of Renewable Resources of the University of Concepción, Chile. The chemicals purchased to assist in high performance liquid chromatography (HPLC) analysis were obtained from Fluka. Milli-Q water was used throughout for the preparation of aqueous solutions or as a component of the mixed water–acetonitrile (HPLC grade) mobile phase in HPLC analysis.

2.2. Reactors and procedures

Laboratory experiments (Lausanne, Switzerland) were carried out in two different reactors: a suntest simulator and a coupled photochemical-biological flow reactor to test the combined treatment. Field test (Almería, Spain) were carried out in two different reactors: a suntest simulator and a coupled photochemical-biological flow reactor to test the combined treatment. Field test (Almería, Spain) were carried out using two types of reactors: a medium concentrating radiation system (Heliosan-type, HM) and a low concentrating radiation system (based on CPC).

2.2.1. Suntest simulator

The photocatalytic experiments were performed using 40 ml Pyrex flask with a cut-off at $\lambda = 290$ nm placed into a Hanau suntest simulator. The radiation source employed was a lamp (AM1) where the radiant total flux (40 mW cm$^{-2}$) was measured with an YSI Corporation powermeter. The lamp has a $\lambda$-distribution with about 0.5% of the emitted photons at wavelengths shorter than 300 nm and about 7% between 300 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum.

2.2.2. Coupled photochemical-biological flow reactor

2.2.2.1. Coaxial photocatalytic reactor

Titanium dioxide supported on glass rings (4 mm length, 4 mm internal diameter) was employed in the photocatalytic reactor shown at the left-hand side of Fig. 2. Immobilization of the catalyst (TiO$_2$ Degussa P-25) was performed by the Laboratory of Renewable Resources of the University of Concepción, Chile according to their previously reported procedure [23,24]. A Philips 36 W (1.20 m long and 26 mm in diameter, TLD 36 W/08) black actinic light source was employed for irradiation in such a way that its center passed through the axis of the reactor. The lamp radiation has a $\lambda$-distribution between 330 and 390 nm centered at 366 nm. The reactor had a total volume of 1.5 l where 0.8 l were illuminated. The runs were carried out at room temperature. The herbicide solution was fed into the system from a 20 l reservoir and was continuously recirculated at 90 l h$^{-1}$ by means of a peristaltic pump through the illuminated part of the reactor. Samples were taken periodically from a mixing-vessel sampling port. The glass rings impregnated of TiO$_2$ floated freely in the space between the light source and the outer wall of the jacketed reactor. During the photocatalytic experiments, the coaxial reactor was covered with an aluminium-coated parabolic device to avoid loss of light by reflecting it through the bulk of the solution. To prepare the ef fluent for the biological
treatment, a conditioning recipient is available between the photocatalytic and the biological reactor, in which, the pH of the phototreated solution can be neutralized, if necessary, by means of NaOH.

2.2.2.2 Biological reactor. The fixed bed reactor (FBR) shown at the right-hand side of Fig. 2 consists of a column of 1 l of capacity containing biolite colonized by activated sludge from a municipal wastewater treatment plant (Vidy, Lausanne, Switzerland). The effluent of the photochemical step was circulated through the column, which operated as an up-flow reactor. To assure a good contact of the phototreated solution with the biomass, the water was recirculated at 6 l h\(^{-1}\). The pH was controlled by a probe and adjusted at 7 by means of HCl or NaOH, depending on the case. The required nutrients (N, P, K, and oligoelements) for the bacterial activity were also added. The aeration was about 150 l h\(^{-1}\) and the O\(_2\) concentration was checked by means of an O\(_2\) probe on the top of the column.

2.2.3 Solar collectors
Solar experiments were carried out at the Plataforma Solar de Almería (PSA), using natural sunlight irradiation. A CPC and a Helioman collector (HM) have been used for the photocatalytic essays. The CPC collector has been described in detail previously [5] and consists of three modules (collector surface, 3.08 m\(^2\), photoreactor volume 22 l, and total reactor volume 39 l) whereas one module consists of 8 tubes. The three modules of the reactor are mounted on a fixed platform inclined 37° (local latitude). The three modules are connected in series and the water flows directly from one to the other and finally to a tank. A centrifugal pump then returns the water to the collectors. At the beginning of the experiments, with collectors covered, the water, TiO\(_2\) powder, and the herbicide are added to the tank and mixed until constant concentration is achieved throughout the system. Then the cover is removed and samples are collected at predetermined times (t). The HM collector consists of a turret on which a platform supporting four parabolic...
trough collectors with an absorber tube in the focus has been placed. The platform is moved by two motors controlled by a two-axis (azimuth and elevation) tracking system. The tracking system consists of a photoelectric cell keeping the aperture plane perpendicular to the solar rays, which are reflected onto the focus (absorber), through which circulates the water to be treated.

Solar ultraviolet radiation (UV) has been determined during the experiments. It is a highly important parameter for the correct treatment of data obtained from solar photocatalytic experiments. A global UV radiometer (KIPP&ZONEN, model CUV3) was used mounted on a 37° fixed-angle platform (the same angle as the CPC’s). The other sensor for the direct UV light (International Light-ESD 400) is mounted on a sun tracking platform. These sensors provide data in terms of global or direct UV solar energy power incident per unit area, W_{UV}{m^{-2}} (UV_{G,n}). Obviously, solar-UV power varies during experiments, made still more noticeable by clouds. With Eq. (1), combination of the data from several days experiments and their comparison with other photocatalytic experiments is possible.

\[ Q_{UV,n} = Q_{UV,n-1} + \Delta t \frac{A_{PCP,HD}}{V_{TOT}} \]  

where \( \Delta t \) = \( t_n - t_{n-1} \) and \( t_n \) is the experimental time for each sample, \( \Delta t \) is the average UV during \( A_{PCP} \) the irradiated surface of collectors (3.08 m²), \( V_{TOT} \) the total volume of the photoreactor (39 l), and \( Q_{UV,n} \) is the accumulated energy per unit of volume (kJ l⁻¹) incident on the reactor for each sample taken during the experiment. For the HM reactor, \( A_{HD} = 29 \text{ m}^2 \), and \( V_{TOT} = 260 \text{ l} \).

2.3 Chemical and biological analysis

At the EPFL, the dissolved organic carbon (DOC) measurements were performed using a TOC analyzer (Shimadzu, model 5050A) with a solution of potassium phthalate as the calibration standard. chemical oxygen demand (COD) was carried out via a Hach-2000 spectrophotometer using dichromate solution as the oxidant in strong acid media. HPLC was carried out in a Varian 9065 unit using a diode array detector between 200 and 400 nm. A Spherisorb silica column ODS-2 was used and the mobile phase (flow: 1 ml min⁻¹) consisted of an acetonitrile/water mixture (50%/50% (v/v)). This technique allows to measure the herbicide concentration in solution. The inorganic ions in the solution were monitored by flow injection analysis (FIA).

Biological oxygen demand (BOD₅) analysis was made by means of a Hg free WTW 2000 Oxytot unit thermostated at 20°C. The Zahn-Wellens biodegradability test [25] was used with bacterial concentration of 1 g l⁻¹. The sludge from the biological activated sludge plant of Lausanne was aerated for 24 h and subsequently centrifuged. The centrifuged sludge was then suspended at 1 g l⁻¹ in the Zahn-Wellens test. During the photochemical pre-treatment, the toxicity was assessed using the Microtox® technique. The bioluminescence of the bacteria Vibrio fischeri in the presence of herbicides was followed as a function of the photochemical treatment time. The toxicity of the sample was determined by measuring the EC₅₀, the effective concentration at which 50% of the light is lost due to compound toxicity.

At the PSA, the concentrations of herbicides were determined using HPLC (Hewlett-Packard model 1050) equipped with a UV detector and a RP-18 column (Lichrocart, i.d. 4 and 150 mm long). The eluent was a methanol/water mixture (50%/50% (v/v)). The TOC was measured directly in slurries by using a Heraeus-Fass Electric TOC-2001 (UV-peroxydisulphate method). Calibration was achieved by using standards of potassium hydrogen phthalate.

3. Results and discussion

3.1 Supported versus suspended TiO₂ catalyst

Employing the coaxial reactor described in Section 2.2.2.1 the photocatalytic degradation of IP (0.2 mmol l⁻¹) with TiO₂ Degussa P-25 coating glass rings was compared with the one using the catalyst suspended in solution. For this comparison, 0.2 g l⁻¹ of TiO₂ Degussa P-25 in suspension was used, which is equivalent to the amount of catalyst deposited on the ~3000 glass rings used to fill out the coaxial reactor treating 1.5 l of solution. As shown in Fig. 3, the kinetic curves of IP degradation behave as a first order process. In both systems, the total elimination of IP is reached in approximately 120 min of photo-
treatment whereas the mineralization reached in the same time is only of about 20%. The degradation kinetics of IP and the DOC evolution in both supported and suspended TiO2 systems are very similar. These results clearly indicate that the catalytic activity of the TiO2 is not reduced when it is immobilized on the inert surface. In addition, supported photocatalyst is rather advantageous for systems under continuous flow, since usual recovering steps such as filtration and decantation can be avoided. Encouraging results were also obtained by Yeber et al. [26] using the same TiO2 impregnated on glass rings for the degradation of cellulose bleaching effluents.

3.2. Supported TiO2 durability

The durability of the catalyst activity was investigated by using the TiO2-impregnated glass rings for the photocatalytic degradation of several compounds. A single batch of glass rings was regularly utilized during 5 months cumulating approximately 300 h of photodegradation experiments on five different compounds. After that, it was observed that the photocatalytic activity of the supported TiO2 for the IP photodegradation remained as high as at the beginning of its use.

The catalytic activity retention is quite high and renders the supported TiO2 very interesting as it does not need to be separated from the treated solution and can easily be held in a technical system and re-used many times.

3.3. Comparison of the photocatalytic degradability via supported TiO2 of four herbicides structurally close to IP

Fig. 4 shows the disappearance of MB, IP, CT, and CB in the coaxial illuminated reactor using supported TiO2. The initial concentration of each compound was of 0.1 mmol l\(^{-1}\).

The initial degradation rates \(v_0\) for the four herbicides in the coaxial reactor are presented in the first column of Table 1. Their photoreactivity can be ranked in the following order: IP > CT > MB > CB. This order indicates that photoreactivity of these herbicides is directly related to the electron-donor or electron-withdrawing character of the different substituents in the herbicides aromatic ring, which can...
activate or deactivate the ring with respect to electrophilic attack of the •OH radical. To explain these results, only the effect of substituents in positions 3 and 4 (see Fig. 1) was taken into account since the substituent in position 1 is similar in all cases.

IP was the most reactive substance due probably to presence of the CH(CH₃)₂ group, which is benzene ring activating and to the absence of halogen substituents (Fig. 1). The other three herbicides contain halogen groups that are considered as deactivating. Some studies [27, 28] concerning the photodegradation of mono-, di-, and tri-chlorophenols indicate that the photocatalytic degradation of these compounds proceeds by the attack of electrophilic species such as •OH and that it should be faster with a greater aromatic ring electron density. Consequently, the degradation rates of the chlorophenols decrease with the degree of chlorination increase. We have tried to explain our results by analogy with this fact. CB has two halogen groups (–Br and –Cl) bounded to the aromatic ring and this could explain its lower reactivity when compared with the other herbicides. Only one halogen group is present in the molecular structure of CT (–Cl) and MB (–Br) and the difference in their photoreactivity is probably due to the presence of a –CH₃ activating group in the CT herbicide. As it is known, the activating character of a –CH₃ group prevails over the deactivating character of a –Cl group explaining why CT reacts faster than MB.

The photocatalytic degradation of these same herbicides was also carried out in irradiated aqueous suspensions of TiO₂ in a suntest simulator (Section 2.2.1) and at pilot scale in a CPC reactor (Section 2.2.3). The initial degradation rates (ν₀) for the four herbicides in the suntest and CPC reactor are also presented in Table 1.

As shown in Table 1, the initial degradation rates of the four herbicides differ between each type of system but can be ranked in the same order independently of the type of reactor.

### Table 1

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Coaxial reactor using supported TiO₂ (mmol l⁻¹ h⁻¹)</th>
<th>Suntest simulator using suspended TiO₂ (mmol l⁻¹ h⁻¹)</th>
<th>CPC collector using suspended TiO₂ (mmol l⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP</td>
<td>0.49</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>CT</td>
<td>0.44</td>
<td>0.19</td>
<td>0.20</td>
</tr>
<tr>
<td>MB</td>
<td>0.38</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>CB</td>
<td>0.31</td>
<td>0.11</td>
<td>0.10</td>
</tr>
</tbody>
</table>

*Conversion from mg kJ⁻¹ to mmol l⁻¹ h⁻¹ is made taking into account that in the CPC reactor, 1 kJ l⁻¹ is equivalent to ~7 min of illumination (see Section 3.6.2).*

3.4. Chemical and biological characteristics of the phototreated IP solution

Before the photocatalytic treatment of IP, the biodegradability of a solution of this compound was tested. From the Zahn-Wellens biodegradability test [25] it has been shown that this herbicide cannot be biologically degraded in the tested conditions, since the DOC of the solution remains at its initial level. This test is carried out under conditions that are similar to those of a wastewater treatment plant using activated sludge. The DOC concentration does not change for this herbicide, even after a period of 28 days. This indicates that bacteria cannot adapt to degrade this herbicide. A parallel control experiment using diethylenglycol (0.5 g l⁻¹) was carried out to test if the sludge was active. The diethylenglycol was in fact degraded as much as 98% in 6 days.

A supplementary test to measure the biodegradation of IP was carried out in batch mode with the FBR shown at the right-hand side of Fig. 2. Even under theoretically favorable conditions as the presence of co-substrates and adapted bacteria, as well as a strict control of pH, temperature, and aeration, this test confirms that IP is non-biodegradable in the tested conditions. Three techniques were used to follow this test: (a) respirometric measurements with an O₂ probe in both the inlet and outlet of the FBR, (b) determination of herbicide concentration by HPLC and (c) measurements of DOC as a function of time.
Fig. 5. Evolution of initial compound, DOC, NO$_3^-$, and toxicity (expressed as $1/EC_{50}$) during the phototreatment of an IP solution (0.2 mmol l$^{-1}$) with supported TiO$_2$ catalyst.

After the photochemical treatment, the biocompatibility of the treated solution was studied to be sure that the photocatalytic process can be used as a pre-treatment, preceding a biological treatment. For this, it is very important to gather information concerning the chemical nature of the solution during the photo pre-treatment following the evolution of the initial compound, the DOC, and the formed ions, as well as the toxicity and the biodegradability. Fig. 5 shows the evolution of IP, DOC, NO$_3^-$, and toxicity for the IP photodegradation in batch mode using the coaxial reactor with supported TiO$_2$ on glass rings.

A very high toxicity increase was observed at the beginning of the treatment, followed by a sharp decrease. This indicates that at the beginning of the photo-assisted pre-treatment the intermediates formed were more toxic than the initial compound. But after 2 h of phototreatment the toxicity of the solution is low and close from those of the initial compound. The ion NO$_3^-$ is generated in the stoichiometric value (24.8 mg NO$_3^-$ l$^{-1}$, corresponding at 100% in Fig. 5) after about 2 h of treatment, indicating the absence in the solution of nitro-compounds. The evolution of DOC shows that the mineralization is only of about 20% when IP is completely eliminated.

A biodegradability study shows that, after phototreatment, the solution resulting from the photodegradation of IP is appropriate for a biological treatment. The ratio BOD$_5$/COD (representative of the biodegradability) was found to be 0 before phototreatment and it increases up to 0.65 after 1 h of pre-treatment (the individual values of BOD$_5$ and COD are of 36 and 55 mg O$_2$ l$^{-1}$, respectively). As a reference, this parameter for biodegradable municipal wastewater is of around 0.4 [11]. It should be noticed that BOD$_5$/COD ratios higher than 0.4 indicate a readily and rapidly degradable solution, while ratios below 0.4 involve the presence of slowly biodegradable compounds.

The chemical observations described above, validated by the concomitant decrease of the toxicity and increase of biodegradability of the treated solution of IP, suggest that the process employing supported TiO$_2$ is a promising pre-treatment method. Therefore, a photochemical-biological coupled flow treatment can be considered for the complete mineralization of this compound.

3.5. Photochemical-biological coupled flow treatment

The coupled photochemical-biological flow reactor described in the experimental section (Fig. 2) was used operating it in semi-continuous mode for the mineralization of an IP aqueous solution. The coupled system developed here employs TiO$_2$ supported on glass rings in the photocatalytic reactor where the pre-treatment of the solution is made. This process is followed by a biological system with immobilized biomass. This physicochemical pre-treatment is necessary to modify the structure of the pollutant by transforming it into non-toxic and easily biodegradable intermediates. This allows the subsequent biological degradation to be achieved in a shorter time and less-expensive way.
The phototreatment stage of the coupled system was intended to obtain a phototreated solution biologically compatible after elimination of the initial bio-recalcitrant compound and the inhibitory intermediates. These requirements, and the information concerning the toxicity and the biodegradability evolution of the phototreated solution of IP, allow us to determine an optimal phototreatment time in the illuminated reactor of the coupled system. This time corresponds to the best compromise between the efficiency of the phototreatment and its cost. The shortest phototreatment time is desired to avoid long irradiation periods and the consequent high electrical consumption. This is important because electricity represents about 60% of the total operational cost of the photochemical reactors [29]. However, if the fixed pre-treatment time is too short, the intermediates remaining in solution could still be structurally similar to the initial bio-recalcitrant compound.

Fig. 6 shows the evolution of the initial compound during the pre-treatment process and the evolution of DOC in both photochemical and biological treatments. At 60 min of phototreatment, when IP is completely eliminated, about 80% of DOC remains in solution. The slow decrease of DOC compared with the IP evolution indicates an accumulation of intermediates. The biodegradability and toxicity tests performed during a photodegradation run in batch mode show that the resulting solution becomes biocompatible when the DOC becomes almost stable and after the quasi-total elimination of IP. Consequently, the optimal time to stop the phototreatment before feeding the treated water to the biological reactor was found to be 1 h. At this stage of the phototreatment, the pH of the solution was around 6.5 with no need of neutralization. Normally, employing photo-Fenton process, neutralization of the solution is necessary because after reaction the acidity of the solution becomes very high. During the biological process the pH must be maintained between 6.5 and 7.5.

IP and its degradation intermediates were followed by HPLC and UV spectrophotometry during the photodegradation process. It was observed that at 1 h the phototreatment depleted IP up to 97% producing aromatic and aliphatic by-products, which were not identified. Fig. 7 shows the UV spectra of phototreated samples taken before the biological treatment and at 10 and 120 min, afterwards. These results confirm the presence of photochemically resulting aromatic and aliphatic intermediates and its decay during the biological treatment. The effective mineralization of the solution during the biological stage was proved by the DOC evolution shown in Fig. 6. The total mineralization could also be obtained via a single photocatalytic process, but this approach is rather expensive due to the high electricity consumption over long irradiation periods.

In the coupled reactor, sequential batches of the phototreatment process were carried out every 60 min that correspond to an input flow rate of 1.51 h⁻¹. This flow rate was maintained during at least 3 days after reaching the steady state to assure the stability of the system during a long time period.

The photoreactor characteristics and the performances of the coupled system are summarized in Table 2.
Table 2
Performances for IP degradation by the coupled photochemical-biological reactor operated in semi-continuous mode

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Photochemical coaxial reactor</th>
<th>Biological reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of reactor (l)</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Input flow rate (l h(^{-1}))</td>
<td>1.5</td>
<td>0.75</td>
</tr>
<tr>
<td>Dilution rate, D (h(^{-1}))</td>
<td>1.0</td>
<td>0.75</td>
</tr>
<tr>
<td>Residence time (h)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Input concentration (mg Cl(^{-1}))</td>
<td>35.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Output concentration (mg Cl(^{-1}))</td>
<td>28.0</td>
<td>2.0</td>
</tr>
<tr>
<td>IP removed (%)</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>DOC removed (%)</td>
<td>20.0</td>
<td>93.0</td>
</tr>
<tr>
<td>Overall efficiency related to DOC removal (%)</td>
<td>95.0</td>
<td></td>
</tr>
</tbody>
</table>

In this coupled system, 100% of the initial concentration of IP and 95% of DOC were removed.

3.6. Perspectives for the coupling of photochemical-biological systems at field pilot scale

3.6.1. Comparison between CPC and HM reactors during the photodegradation of IP via suspended TiO\(_2\)

This part of the paper focuses on the comparison of performance of two types of solar collectors, HM and CPC, with regard to the photodegradation of IP via suspended TiO\(_2\). Fig. 8 shows the linear relation between -ln(C/C\(_0\)) and Q\(_{UV}\) for the IP herbicide disappearance in the reactors. In both cases, the kinetics of IP degradation are of apparent first order, with a rate constant (k\(_{app}\)) equal to 0.58 and 0.11 l kJ\(^{-1}\) for the CPC and HM reactors, respectively.

Previous research indicates that the degradation rate of p-NTS [30] is around three times higher than those observed in the parabolic HM collectors. Fig. 8 shows that the degradation rate of IP is five times higher in the CPC reactor than in the HM reactor. There are different loss factors (n) that affect the efficiency of both CPC and HM collectors, which could partially explain the difference in the degradation rate of IP indicated above. These factors have been previously described in detail [31]. The definition of each of these loss factors and their values are summarized as follows.

1. The n\(_s\) is a loss factor originated from the error produced during solar tracking by the control system collector's. The value of this factor is 0.92 for the HM collector. The CPC collector has not this system and the factor may be considered as 1.0.

2. The n\(_c\) is a loss factor due to the construction characteristics of the solar collectors. Its value is 0.91 and 1.0 for HM and CPC, respectively.
3. The $n_r$ is related with the reflectivity of the aluminized surface of the collectors. Its value is 0.60 for HM and 0.90 for CPC, respectively.

4. The $n_t$ is a loss factor due to the transmissivity of the absorber tubes. Its value is 0.90 and 0.91 for HM and CPC, respectively.

In addition, the ratio between the photocatalytic reaction rate and the intensity of radiation coming inside the reactor changes with the radiation power in a different way depending of the type and geometry of the photoreactor. It is generally accepted that in a CPC collector the reaction rate is directly proportional to the intensity ($I$) of illumination ($r = kI$). In contrast, since the intensity obtained with the HM collectors is about 10.3 suns, the reaction rates may be correlated to the square root of the intensity of illumination ($r = k'\sqrt{I}$) or $r^2 = k'I$.

Furthermore, the CPC collectors are able to capture both, diffuse and direct UV sunlight. In contrast, a concentrating design like that of the HM reactor, benefits only from the direct UV radiation, which could be drastically decreased on a cloudy day [32,33]. The diffuse component can represent 50% of the total available UV light, even on a clear day. This phenomenon could influence the photodegradation of the same compound in a different ways since photocatalytic reaction pathways and degradation intermediates could be different depending on light incidence. Thus, we could conclude that the nature of the compound is also an important factor to be taken into account when the efficiency of different reactors are compared towards the degradation of organic substances.

All the factors presented above rend the CPC collector more efficient than the HM collector. This fact, together with low manufacturing, installation, and maintenance costs, and easy operation of the CPC collectors compared with the HM reactors, suggest that the former ones are, at present, the best way to use the solar technology.

3.6.2. Kinetics of the disappearance of IP by different advanced oxidation processes

Using the CPC photoreactor, various experiments were carried out in order to compare the efficiency of the solar photocatalytic treatment of IP based on the photo-Fenton system and TiO$_2$ photocatalysis. Fig. 9 shows the evolution of TOC when a solution of IP (0.15 mmol L$^{-1}$) is reacted using direct sunlight in different degradation systems under aerobic conditions: UV/TiO$_2$, UV/TiO$_2$/H$_2$O$_2$, and UV/Fe$^{3+}$/H$_2$O$_2$. It is not plotted as a function of the residence time in the CPC reactor, but as a function of the accumulated energy per unit of volume (kJ L$^{-1}$), in order to correct any possible variation of the radiant flux. The energy accumulated ($Q_{UV}$) on the reactor per each sample was estimated using Eq. (1).

![Fig. 9](image-url) Evolution of TOC during the degradation of IP in different degradation systems as a function of accumulated energy: Fenton (▲), TiO$_2$ (■), TiO$_2$ + H$_2$O$_2$ (●); IP (0.15 mmol L$^{-1}$), H$_2$O$_2$ (30 mmol L$^{-1}$), Fe$^{3+}$ (1 mmol L$^{-1}$), TiO$_2$ (0.2 g L$^{-1}$).
TiO₂ catalyst. The TiO₂ absorbs in the UV light with a wavelength <387 nm (4% of the solar irradiation) while the Fenton system can be active to wavelengths up to 600 nm (35% of the solar irradiation).

As shown in Fig. 9, the addition of H₂O₂ to the UV/TiO₂ system does not have a beneficial effect on the mineralization of the IP solution. The effect of this strong electron acceptor depends on its concentration [34]. An optimal H₂O₂/pollutant molar ratio between 10 and 100 has been proposed by several authors [35,36]. When this ratio is higher than 100, an inhibiting effect is detected. In our case, initial IP and H₂O₂ concentrations of 0.15 and 30 mmol l⁻¹, respectively give an inhibitory ratio of 200.

Even if the photo-Fenton reaction is the most efficient process for the mineralization of the IP solution, both homogeneous and heterogeneous photocatalysis are considered as suitable methods to reach the complete decay of IP in the solution. HPLC analyses indicate that with less than 5 kJ per liter of accumulated energy, the compound responsible for the non-biodegradability of the solution (IP), is completely degraded in all systems. We decided to go further into the study of the TiO₂ photo-assisted process since this catalyst is not sacrificed in the catalytic reaction and can be separated from the treated water. This is very important when an industrial application is contemplated since clean treated water could be drained away and TiO₂ recycled. Different procedures of filtration or sedimentation have been published for this purpose [37,38].

Fig. 10 shows the degradation of a solution of IP in the CPC reactor. When IP is completely eliminated, about 80% of the DOC remains in solution. This slow decrease of the DOC indicates an accumulation of intermediates. It was demonstrated that, at laboratory scale, the biocompatibility of the treated solution is attained when the initial compound is completely eliminated and the DOC removal is of about 20% (see Section 3.4). By extrapolation of these results we can consider that, at pilot scale, a phototreated solution of IP is also biocompatible after 10 kJ l⁻¹ of accumulated energy in the CPC reactor. Thus, a coupled CPC-biological system at pilot scale could be envisaged to completely mineralize an IP solution.

As shown in Fig. 10, the energy necessary to reach a complete mineralization of the IP solution is far more than three times the energy necessary for IP elimination. In this context, the implementation of a coupled system could reduce the cost of the treatment. In a sunny day in Almería with solar UV radiation average of 30 W m⁻², 1 kJ l⁻¹ is equivalent to approximately 7 min of illumination in the CPC reactor employed for this experiment (1 kJ l⁻¹ = Δt × 30 W m⁻² × 3 m²/39 l). Thus, 39 l of IP-contaminated water can be treated in approximately 1 h of phototreatment in a sunny day employing the CPC reactor. Complete mineralization of the same solution would take longer than 3 h.

These encouraging results as well as those concerning the using of immobilized TiO₂ open new possibilities for the coupling of TiO₂ photo-assisted and biological processes, at pilot scale, employing both supported TiO₂ and bacteria. The main advantage of this fixed system is that a separation procedure of the catalyst is not necessary rendering more economic and simpler the operation of both reactors.

![Degradation of IP (0.1 mmol l⁻¹) in a CPC reactor. Evolution of the initial compound and TOC.](image-url)
4. Conclusions

The photodegradation kinetics of IP employing suspended or supported TiO$_2$ systems are very similar indicating that the activity of the TiO$_2$ is not reduced when it is immobilized on an inert surface like the glass rings used in this work. After 300 h of photodegradation experiments using the same single batch of impregnated glass rings, it was verified that the activity of the supported TiO$_2$ was not affected. The level of catalytic activity retention is quite high and shows that besides supported TiO$_2$ does not need to be separated from the treated solution, it can be re-used many times, which represents another added advantage in favor of the use of supported TiO$_2$.

The order of photodegradation (IP $>$ CT $>$ MB $>$ CB) found for the four phenylurea herbicides using the coaxial reactor and supported TiO$_2$ indicated that their photoreactivity are directly related to the donor or withdrawing effect of the different substituents in the aromatic ring of each herbicide. This same order of photoreactivity was found when the same herbicides were degraded in other two types of reactor and using suspended TiO$_2$. This fact indicates that the photoreactivity of these four herbicides is independent of the system employed for their photodegradation.

This study demonstrates the usefulness of the photo-assisted TiO$_2$ process as pre-treatment method preceding a biological treatment for the complete mineralization of non-biodegradable organic substances. The photodegraded solution of IP is biologically compatible and its complete mineralization can be performed by biological means. The coupled photo-chemical and biological flow reactor operated in semi-continuous mode seems to be an efficient system for the mineralization of the IP solution. The primary degradation efficiency expressed as percentage of IP removed was 100% and the mineralization efficiency was 95%. The coupled system developed in his work employs TiO$_2$ supported on glass rings in the photocatalytic coaxial reactor and fixed bacteria on biolite. These fixed components renders this coupled technology for the treatment of wastewater more economic and simpler.

The field experiments under direct sunlight using solar collectors such as HM and CPC demonstrate that the solar photocatalytic treatment is effective for the purification of water contaminated by herbicides. However, different factors and the low manufacturing, installation, and maintenance costs, and easy operation of the CPC collectors compared with the HM reactors, suggest that the former ones are, at present, the best way to use the solar detoxification technology.

Using the CPC photoreactor, it was demonstrated the utility of the heterogeneous photocatalysis based on TiO$_2$ as a pre-treatment method that can be followed by a biological treatment. Further investigations are needed concerning the biological treatment at pilot scale of the solution resulting from the degradation of IP. From this study, a coupled CPC-biological system could be envisaged to complete the mineralization of herbicide solutions.

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